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Geochemistry and Sm–Nd chronology of a Stannern-group eucrite, Northwest Africa 7188

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Abstract

We report the results of a detailed study of the basaltic eucrite Northwest Africa (NWA) 7188, including its mineralogical and bulk geochemical characteristics, oxygen isotopic composition, and $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ mineral isochron ages. The texture and chemical composition of pyroxene and plagioclase demonstrate that NWA 7188 is a monomict eucrite with a metamorphic grade of type 4. The oxygen isotopic composition and the Fe/Mn ratios of pyroxene confirmed that NWA 7188 belongs to the howardite-eucrite-diogenite meteorite suite, generally considered to originate from asteroid 4 Vesta. Whole-rock TiO_2 , La, and Hf concentrations and a CI chondrite-normalized rare earth element pattern are in good agreement with those of representative Stannern-group eucrites. The $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ isochrons for NWA 7188 yielded ages of 4582 ± 190 and 4554^{+17}_{-19} Ma, respectively. The closure temperature of the Sm–Nd system for different fractions of NWA 7188 was estimated to be >865 °C, suggesting that the Sm–Nd decay system has either been resistant to reheating at ~ 800 °C during the global metamorphism or only partially reset. Therefore, the ^{146}Sm – ^{142}Nd age of NWA 7188 corresponds to the period of initial crystallization of basaltic magmas and/or global metamorphism on the parent body, and is unlikely to reflect Sm–Nd disturbance by late reheating and impact events. In either case, NWA 7188 is a rare Stannern-group eucrite that preserves the chronological information regarding the initial crustal evolution of Vesta.

1 INTRODUCTION

2 Eucrites are differentiated achondrites and belong to the howardite–eucrite–
 3 diogenite (HED) suite of meteorites that most likely originated from the crust of asteroid
 4 4 Vesta (McCord et al. 1970; Consolmagno and Drake 1977; Binzel and Xu 1993; Drake
 5 2001; McSween et al. 2011, 2013; Mittlefehldt 2015). The linkage between the HED
 6 meteorites and Vesta was originally proposed in the 1970s (e.g., McCord et al. 1970)
 7 based on similarities between laboratory and astronomically observed visible and near-
 8 infrared spectra. The linkage between the HEDs and Vesta obtained additional support as
 9 a result of lithological mapping of Vesta’s surface using the visible and infrared mapping
 10 spectrometer on board NASA’s Dawn spacecraft (De Sanctis et al. 2012). From an orbital
 11 dynamics perspective, it is difficult for the fragments ejected from Vesta in the main belt
 12 to come to Earth through Jovian or secular resonances directly. However, Vestoids—
 13 which are small asteroids (< 10 km) believed to have originated from Vesta based on
 14 Vesta-like spectra—could solve this problem by expanding the area from which
 15 fragments of Vesta can be ejected to Earth (McSween et al. 2011).

16 Vesta is generally thought to have experienced large-scale melting that led to core–
 17 mantle segregation and silicate differentiation (Schiller et al. 2011). This probably
 18 occurred a few million years (Myr) after Solar System formation, based on the evidence
 19 from chronometers using short-lived radionuclides, such as ^{26}Al ($t_{1/2} = 0.7$ Myr), ^{53}Mn
 20 ($t_{1/2} = 3.7$ Myr), and ^{182}Hf ($t_{1/2} = 9$ Myr). The ^{182}Hf – ^{182}W ages of eucrites and diogenites
 21 suggest that metal segregation on Vesta occurred ~ 1 – 4 Myr after the formation of calcium
 22 and aluminum-rich inclusions (CAIs) (Kleine et al. 2004, 2009; Quitté and Brick 2004;
 23 Touboul et al. 2015). In contrast, the ^{53}Mn – ^{53}Cr and ^{26}Al – ^{26}Mg whole-rock isochron ages
 24 of eucrites and diogenites suggest that global silicate mantle differentiation continued for
 25 approximately 2–10 Myr after CAI formation (Lugmair and Shukolyukov 1998; Bizzarro
 26 et al. 2005; Trinquier et al. 2008). Although analytical uncertainties are large, the ^{147}Sm –
 27 ^{143}Nd and ^{176}Lu – ^{176}Hf whole-rock isochron ages of eucrites (4587 ± 150 and 4532 ± 170
 28 Ma, respectively), both of which most likely indicate the timing of crust formation, are
 29 consistent with each other (Bouvier et al. 2015). The sequential processes of partial (15–
 30 20%) or total melting and differentiation homogenized the oxygen isotope compositions
 31 among HED meteorites (Greenwood et al. 2005, 2017). In addition, the Fe/Mn ratios in
 32 pyroxene are relatively uniform among basaltic eucrites ($\text{Fe/Mn} = 30 \pm 2$), because Fe
 33 and Mn do not fractionate during the magmatic process (Mittlefehldt et al. 1998; Papike
 34 1998; Papike et al. 2003).

35 Eucrites mainly consist of pyroxene and plagioclase and are petrographically
 36 classified into basaltic and cumulate eucrites. Basaltic eucrites are composed of pigeonite

and plagioclase with a subophitic texture, indicating that they crystallized near the surface. In contrast, cumulate eucrites—which are composed of orthopyroxene and plagioclase—have a gabbroic texture and are therefore considered to have crystallized more slowly, from a residual melt, almost certainly at a deeper level in Vesta than the basaltic eucrites (McSween et al. 2011). Based on the whole-rock Mg/(Mg + Fe) molar ratio and the incompatible element concentrations, basaltic eucrites are further classified into four distinct chemical groups: main group, Nuevo Laredo-group, Stannern-group, and residual eucrites (BVSP 1981; Warren and Jerde 1987; Yamaguchi et al. 2009). The Nuevo Laredo-group eucrites are characterized by lower Mg/(Mg + Fe) ratios than those of the main-group and Stannern-group eucrites (Mittlefehldt 2015). On the other hand, the Stannern-group eucrites are characterized by having higher Ti and incompatible element concentrations than those of the combined main-group–Nuevo Laredo-group eucrites. In CI chondrite-normalized rare earth element (REE) diagrams, the Stannern-group eucrites show variable yet nearly parallel REE patterns with distinctive negative Eu anomalies

(Eu/Eu*; $\text{Eu}^* = \frac{\text{Sm}_{\text{CI chondrite-normalized}} + \text{Gd}_{\text{CI chondrite-normalized}}}{2}$), where the abundance

of La ranges from 17 to $28 \times \text{CI}$ (Shimizu and Masuda 1986; Barrat et al. 2007). The residual eucrites (e.g., Dar al Gani 945), which most likely represent a complement to the Stannern-group eucrites, are characterized by depletions in light-REEs (LREEs; La–Sm) relative to heavy-REEs (HREEs; Gd–Lu) coupled with positive Eu anomalies in the CI chondrite-normalized REE patterns (Yamaguchi et al. 2009). This compositional diversity amongst eucrites provides an important clue to understanding the igneous differentiation processes on Vesta. In addition to the above-mentioned geochemical classification, nearly all of the basaltic eucrites are classified into one of seven metamorphic grades (types 1–7) on the basis of pyroxene petrographic and compositional criteria (Takeda and Graham 1991; Yamaguchi et al. 1996). The Stannern-group eucrites commonly have metamorphic grades of types 1–4, indicative of very low to moderate metamorphism, whereas most of the main-group eucrites are classified as types 5–7 because they are highly metamorphosed with peak temperatures of $\sim 1000^\circ\text{C}$ (Takeda and Graham 1991).

Most recently, the desert meteorite Northwest Africa (NWA) 7188, which had been simply categorized as a basaltic eucrite (Ruzicka et al. 2015), was found to be a new member of monomict Stannern-group eucrites (Kagami et al. 2017, 2018). In addition, petrological observations revealed that NWA 7188 had a very low shock stage and a low degree of terrestrial weathering, making it a suitable specimen to investigate in detail the origin of the Stannern-group eucrites. In this study, we have conducted detailed

geochemical analyses of NWA 7188, including major and trace element abundances, oxygen isotope measurements of the bulk rock, mineralogical analysis, as well as determining $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ isochron ages for mineral separates. Sm–Nd systematics have a number of advantages for eucrite dating: 1) Sm and Nd are REEs that are not significantly fractionated from each other during secondary alteration, and 2) the Sm–Nd systematics are not easily reset by thermal metamorphism compared to the U–Pb, ^{87}Rb – ^{87}Sr , and ^{39}Ar – ^{40}Ar systems (Bogard and Garrison 2003). The goal of this study was to understand the petrogenesis of NWA 7188 in order to provide crucial constraints on the thermal evolution of the Stannern-group eucrites on Vesta.

SAMPLES

NWA 7188 is a hot desert meteorite found in 2011, with a total mass of ~455 g. It was originally classified as a basaltic eucrite based on petrological observations and mineralogical data. NWA 7188 consists of exsolved pigeonite, calcic plagioclase, silica polymorphs, ilmenite, and troilite (Ruzicka et al. 2015). The pyroxenes have clinopyroxene lamellae with an FeO/MnO ratio of 32 within a low-Ca pyroxene host with an FeO/MnO ratio of 33–35.

In this study, we investigated three commercially sourced specimens of NWA 7188, which were named specimens A (6.9 g), B (24.8 g), and C (79.8 g). The fusion crust covering the surface of specimens B and C was carefully removed using a micro-drill equipped with a ceramic grinding stone. In addition, the brown altered part near the rim of these specimens was discarded. Because the three specimens had a similar texture, specimen A was used for textural and mineralogical observations and O isotope analyses, while specimens B and C were used for chemical and Nd isotope analyses.

ANALYTICAL METHODS

Figure S1 shows a flowchart for the experimental work conducted as part of this study. Although NWA 7188 has two distinct textures, we used sample batches that included both lithologies for the analyses of bulk chemical composition, isotopic systematics and Sm–Nd isochron studies. It is reasonable to include both textural types because we have been able to confirm that they are co-genetic (see the Petrology and Mineral Chemistry in Results section). The procedures used for individual experiments are described in detail below.

Textual and Mineralogical Observations

Specimen A was mounted in an epoxy resin disk and polished with 3, 1, and 1/4 μm diamond paste to make a thick section (Fig. S1). The polished thick section was examined using a scanning electron microprobe (SEM; S-3400N, Hitachi High-Technologies, Japan) instrument equipped with an energy dispersive spectrometer (EDS) at the Tokyo Institute of Technology (Tokyo Tech). Elemental mapping of Al, Ca, Fe, Mg, P, Si, Ti, and Zr was undertaken using the SEM-EDS to identify major minerals such as plagioclase and pyroxene. In addition, a field-emission-type electron microprobe analyzer (FE-EPMA; JXA-8530F, JEOL, Japan) installed at Tokyo Tech was used to obtain the elemental maps for Zr, Ca, Ti, and Fe with an accelerating voltage of 15 kV and a beam current of 30 nA in order to find zircon and ilmenite minerals. The chemical compositions of pyroxene and plagioclase were also measured by employing FE-EPMA analyses with an accelerating voltage of 15 kV, a beam current of 10 nA, and an analytical beam spot of 2–3 μm . The following samples supplied from JEOL were used as standards of FE-EPMA analyses: SiO_2 for Si, TiO_2 for Ti, Al_2O_3 for Al, Fe_2O_3 for Fe, MnO, for Mn, MgO for Mg, CaSiO_3 for Ca, $\text{NaAlSi}_3\text{O}_8$ for Na, and KAlSi_3O_8 for K. The modal abundance of major mineral phases in NWA 7188 was determined using image analysis software (JMicroVision, Switzerland; Roduit 2008). Elemental maps for Fe, Si, Al, and Mg were combined and divided into quarters. We counted ca. 330 points per image, with a size of 5120 pixels \times 2577 pixels (1.1 cm \times 5.6 cm).

Sm–Nd Dating

For the application of Sm–Nd radiometric dating, specimens B and C-1 were crushed and sieved into four fractions: G1) 250–500 μm , G2) 106–250 μm , G3) 45–106 μm , and G4) <45 μm (Fig. S1). The fractions G2–G4 were separated into magnetic and non-magnetic mineral fractions with a neodymium magnet. Then, grains of pyroxene and plagioclase were handpicked from the magnetic and non-magnetic fractions of G2,

respectively. All of these samples were cleaned with distilled acetone and Milli-Q water and then powdered using an agate mortar and pestle.

The chemical procedures for Sm–Nd dating are described in detail elsewhere (Yokoyama et al. 1999; Kagami and Yokoyama 2016; Fukai et al. 2017), here we give an outline summary of the methodology followed in this study. The powdered sample of G1 was weighed in a polytetrafluoroethylene (PTFE) insert (50 mL volume) of a high-pressure digestion system, DAB-2 (Berghof, Germany), together with 30 M HF (AAS grade with distillation, Kanto Chemical, Japan) and 16 M HNO₃ (EL grade, Mitsubishi Chemical, Japan). The sample was dissolved in the digestion system at 225 °C for 48 h to ensure complete dissolution of refractory minerals such as zircons. After the sample dissolution, 12 M HClO₄ (AA–100 grade, TAMA Chemicals, Japan) was added to the sample solution. In contrast, the powdered samples of the G2–G4 fractions were weighed into PTFE vessels (7 mL) together with 30 M HF, 16 M HNO₃, and 12 M HClO₄. The sample solutions of the G1–G4 fractions containing HF, HNO₃, and HClO₄ were subsequently heated in a stepwise fashion at 120 °C for 12 h, 165 °C for 16 h, and 195 °C until dryness. Next, the sample was re-dissolved in 12 M HClO₄ and treated in the same manner as described above to suppress the formation of insoluble fluorides. The dried sample was dissolved with 6 M HCl (EL grade, Mitsubishi Chemical, Japan), which was then dried at 120 °C. The sample was finally dissolved in 1 M HCl.

For the determination of Sm/Nd ratios of individual fractions, a ~10% aliquot of the sample solution was accurately weighed in a clean Teflon vessel and mixed with the ¹⁴⁵Nd- and ¹⁴⁹Sm-enriched spike solutions. After the removal of potential interfering elements by passing the sample solution through an extraction chromatographic resin TRU (50–100 µm; Eichrom, USA), the Nd and Sm concentrations were determined by the isotope dilution (ID) method using a quadrupole type ICP-MS instrument (X-Series 2, Thermo Fisher Scientific, USA) installed at Tokyo Tech (Kagami and Yokoyama 2016).

The remaining ~90% of the sample solution was used for high-precision Nd isotope measurements by thermal ionization mass spectrometry at Tokyo Tech (TIMS; Triton *plus*, Thermo Fisher Scientific, USA). Prior isotopic analysis, a three-step column chemistry procedure utilizing a cation exchange resin and an extraction chromatographic resin (Ln Resin, Eichrom, USA) was undertaken to purify Nd (Kagami and Yokoyama 2016). Subsequently, the ¹⁴²Nd/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd ratios were determined using a dynamic multi-collection method with a two-jump cup configuration in a single measurement (Fukai et al. 2017). The instrumental mass fractionation was corrected by the exponential law and normalized to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 and ¹⁴⁶Nd/¹⁴⁵Nd = 2.072016 (Boyet and Carlson, 2005) for ¹⁴²Nd/¹⁴⁴Nd and ¹⁴³Nd/¹⁴⁴Nd, respectively. The reproducibility of the

$^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the standard, JNdi-1 (500 ng), were 6.5 ppm and 5.2 ppm (2SD), respectively. The $^{142}\text{Nd}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios measured on JNdi-1 during sample measurements in this study are equal to 1.141837 ± 7 and 0.512102 ± 3 , respectively. The total procedural blank for Nd (~ 36 pg) was negligible compared with the amount of Nd used in a single isotopic measurement (> 100 ng). Sm–Nd ages were calculated using Isoplot 3.6 (Ludwig 2009).

Determination of Major and Trace Element Abundances

The bulk chemical compositions of five major elements (Mg, Ca, Fe, Ti, and Mn) and twenty-six trace elements (Rb, Sr, Zr, Nb, Y, Cs, Ba, lanthanoids, Hf, Ta, Pb, Th, and U) for NWA 7188 were determined by using powdered samples from specimens C-2-1 and C-2-2 (Fig. S1). These specimens were cleaned with distilled acetone and Milli-Q water and then powdered using an agate mortar and pestle. Subsequently, C-2-2 was cleaned with distilled acetone and Milli-Q water once again. In addition to NWA 7188, we prepared a reference rock material BHVO-2 (Basalt, USGS, USA) for evaluating the accuracy of the analyses.

Approximately 50 mg of the powdered sample was weighed in a PTFE insert of DAB-2 together with two types of mixed-spike solutions (^{113}In – ^{203}Tl and ^{91}Zr – ^{179}Hf) and a ^{49}Ti spike solution. Subsequently, 0.2 mL Al solution (~ 10000 $\mu\text{g/g}$, Agilent Technologies, USA) was added to achieve full recoveries of HFSEs (Tanaka et al. 2003). The sample was dissolved with 30 M HF in the pressure digestion system at 225 °C for 48 h. After the dissolution, the sample solution was dried and dissolved with 5 mL 0.5 M HF. The sample solution, containing insoluble fluorides, was thoroughly shaken and homogenized using an ultrasonic bath until it became a milky suspended solution without visible precipitates. Immediately after the homogenization, an $\sim 5\%$ aliquot of the suspended solution was transferred to a polypropylene tube and centrifuged. The supernatant liquid was diluted with 0.5 M HF and used for the measurement of high field strength elements (HFSEs; Ti, Zr, Nb, Hf, and Ta) using ICP-MS by the ID method for Ti, Zr, and Hf and by the calibration curve method for Nb and Ta. We used a custom-made mix standard solution (Cat. No. XSTC-3493-100, SPEX CertiPrep, USA) containing HFSEs in 1.7% HF (Ti: 4964 ± 30 $\mu\text{g/g}$, Zr: 98.8 ± 0.5 $\mu\text{g/g}$, Nb: 9.86 ± 0.05 $\mu\text{g/g}$, Hf: 2.96 ± 0.06 $\mu\text{g/g}$, Ta: 1.00 ± 0.02 $\mu\text{g/g}$) for the standard material. Typical analytical reproducibility for HFSEs was less than 2% (2SD).

For the determination of major and trace elements, excluding HFSEs, the remainder of the suspended sample solution was transferred to a Teflon vessel with the addition of 12 M HClO_4 and 16 M HNO_3 , which was heated in a stepwise fashion (120 °C for 12 h,

165 °C for 16 h, and 195 °C until dryness). This procedure was repeated twice to suppress the formation of insoluble fluorides. After the treatment with 6 M HCl, the sample was diluted with 0.5 M HNO₃ to measure major and trace elements, excluding HFSEs, by ICP-MS. The concentrations of major and trace elements, excluding HFSEs, were determined by the calibration curve method coupled with the internal standardization using ¹¹³In and ¹¹³In–²⁰³Tl, respectively (Yokoyama et al. 2017). We used a rock reference material, JB-3 (basalt, Geological Survey, Japan), as the standard in the determination of major and trace elements, excluding HFSEs. The concentrations for JB-3 reported by Kon and Hirata (2015) were used here. Analytical reproducibility was typically less than 2% for REE, 4% for Mg, Ca, Fe, Mn, and trace elements, excluding REEs and Pb, and 14% for Pb (2SD).

Oxygen Isotope Analyses

Oxygen isotope analysis was carried out using an infrared laser-assisted fluorination system at the Open University (Miller et al. 1999; Greenwood et al. 2017). An approximately 200 mg piece of specimen A was crushed and homogenized and two aliquots of this powder, each ~2 mg, were loaded for oxygen isotope analysis. Oxygen gas was released by heating in the presence of BrF₅ and then purified by passing it through two cryogenic nitrogen traps and over a bed of heated KBr. The purified oxygen gas was analyzed using a MAT 253 dual inlet mass spectrometer (Thermo Scientific, USA). Overall system precision, as defined by replicate analyses of our internal obsidian standard (n = 38), is ±0.053‰ for δ¹⁷O (2σ); ±0.095‰ for δ¹⁸O (2σ); ±0.018‰ for Δ¹⁷O (2σ) (Starkey et al. 2016).

Oxygen isotopic analyses are reported in standard δ notation, where δ¹⁸O has been calculated as: δ¹⁸O = [(¹⁸O / ¹⁶O)_{sample} / (¹⁸O / ¹⁶O)_{VSMOW} - 1] × 1000 (‰) and similarly for δ¹⁷O using the ¹⁷O / ¹⁶O ratio. Δ¹⁷O, which represents the deviation from the terrestrial fractionation line, has been calculated using the linearized format of Miller (2002):

$$\Delta^{17}\text{O} = 1000 \ln(1 + \delta^{17}\text{O}/1000) - \lambda 1000 \ln(1 + \delta^{18}\text{O}/1000)$$

where λ = 0.5247, which was determined using 47 terrestrial whole-rock and mineral separate samples (Miller et al. 1999; Miller 2002).

RESULTS

Petrology and Mineral Chemistry

In each specimen of NWA 7188, at least two distinct textures with different grain sizes can be recognized: fine-grained (FG) and coarse-grained (CG) crystalline areas. These textures are separated by a boundary that can be observed under a stereoscopic microscope (Fig. S2a). The FG area has a subophitic texture composed of lath shaped plagioclase and anhedral pyroxene (Fig. 1a). In addition, the FG area partly contains regions that are composed of fine-grained micro-minerals with sizes of several tens of μm . The CG area is composed of lath shaped plagioclase crystal of up to $0.5 \times 2.6 \text{ mm}$ and pyroxene of up to $1.0 \times 2.3 \text{ mm}$.

The SEM observations and elemental maps obtained from FE-EPMA revealed that the FG area contains mesostasis-rich regions including a silica mineral (possibly tridymite), troilite, Ca-phosphate mineral, and ilmenite (Fig. 1b). In addition, tiny zircons ($5\text{--}20 \mu\text{m}$) exist in contact with ilmenite, plagioclase, and pyroxene (Fig. 1c). The elemental maps obtained from SEM and EPMA analyses indicated that NWA 7188 consists of pyroxene (49 vol%), plagioclase (44 vol%), silica minerals (5 vol%), and the other accessory minerals (ilmenite, spinel, Ca-phosphate mineral, troilite, and zircon) (Fig. S2b).

The chemical composition of pyroxene and plagioclase in the FG and CG areas are listed in Table 1. In the Ca–Mg–Fe ternary phase diagram (Fig. 2a), the composition of pyroxene in the CG area ranges from $\text{Wo}_{3.94}\text{En}_{33.9}\text{Fs}_{62.2}$ to $\text{Wo}_{26.1}\text{En}_{29.6}\text{Fs}_{44.3}$ ($n = 13$), while those in the FG area show a larger variation with an overlap with the CG area ($\text{Wo}_{4.22}\text{En}_{34.1}\text{Fs}_{61.7}$ – $\text{Wo}_{40.4}\text{En}_{29.0}\text{Fs}_{30.6}$; $n = 16$). Overall, the compositional variation of pyroxene trends from pigeonite to augite, implying that NWA 7188 should be classified as an ordinary or equilibrated eucrite (Reid and Barnard 1979; Pun and Papike 1996). The Ca–Fe pyroxene compositional trends in the FG and CG areas are closely similar, suggesting that NWA 7188 is a monomict eucrite.

We estimate the equilibration temperature by using the QUILF (quartz-ulvöspinel-ilmenite-fayalite) two-pyroxene geothermometer (Andersen et al. 1993). The geothermometer can be applied to augite lamella in pigeonite, which exists in NWA 7188 as explained below. The calculation of the equilibration temperature requires the Wo and En values in the FG and CG areas, which are summarized in Table 1. The equilibration temperatures determined by QUILF calculation for pyroxene are $896 \pm 60 \text{ }^{\circ}\text{C}$ and $907 \pm 44 \text{ }^{\circ}\text{C}$ in the FG and CG areas respectively and so are essentially indistinguishable from each other. This suggests that the two lithologies originated from the same protolith (i.e., monomict). This petrographic variety in monomict basaltic eucrites, for example

Stannern, NWA 4523, and Millbillillie, has already been reported (Barrat et al. 2007; Yamaguchi et al. 1994).

Most pigeonite grains in NWA 7188 have sub- μm augite lamellae, with the width near the rim being thicker than that of lamellae near the core (Fig. 1d). NWA 7188 can be classified as type 4 due to the characteristics mentioned above and the presence of remnant Ca-zoning, similar to that reported by Yamaguchi et al. (1996) in Stannern pyroxenes (type 4). Figure 3 shows that the Fe/Mn ratios of pyroxene in NWA 7188 range from 29.0 to 35.3 with a mean value of 32.3 ($n = 29$), which is consistent with those of the other basaltic eucrites.

The composition of plagioclase in the FG area range from $\text{Or}_{1.69}\text{An}_{78.0}\text{Ab}_{20.4}$ to $\text{Or}_{0.47}\text{An}_{90.7}\text{Ab}_{8.81}$ ($n = 14$), and those in the CG area range from $\text{Or}_{1.93}\text{An}_{77.0}\text{Ab}_{21.1}$ to $\text{Or}_{0.35}\text{An}_{86.2}\text{Ab}_{13.4}$ ($n = 22$) (Fig. 2b). The chemical composition of plagioclase in FG and CG areas are similar to each other, which have a large variation of An content (14 mol%; An_{77-91}) compared with most other basaltic eucrites with the variation of An content (about 5–10 mol%) (Mayne et al. 2009). This result suggests that plagioclase (Si and Al in albite-anorthite substitution) were not equilibrated.

Bulk Chemical Compositions

Major, minor, and trace element compositions of a bulk sample of NWA 7188 are shown in Table 2, while those of the reference rock BHVO-2 are listed in Table S1 with the values reported previously. The concentrations of major and trace elements in BHVO-2 obtained in this study are in good agreement with those reported in Kon and Hirata (2015), confirming the accuracy of our measurements. The results of Ti and trace elements for C-2-1 and C-2-2 are consistent with each other. This result confirms that the washing procedure for C-2-1 effectively removed the terrestrial materials that were physically adsorbed onto the rock surface, although inter-mineral redistribution of elements due to terrestrial weathering must be separately evaluated (see the discussion). In the following, the mean values of C-2-1 and C-2-2 for individual elements are used as concentrations representing the bulk chemical composition of NWA 7188.

The concentrations of FeO^{T} and MgO in NWA 7188 are 17.2 wt.% and 5.99 wt.%, respectively, which gives $\text{FeO/MgO} = 2.88$ (Table 2). The concentrations of TiO_2 (0.97 wt.%), La (5.20 $\mu\text{g/g}$), and Hf (2.49 $\mu\text{g/g}$) in NWA 7188 are higher than those in most basaltic eucrites, whereas the FeO/MgO ratio is within the range of the other eucrites (2.3–3.7; Fig. 4). Figure 5 shows the CI chondrite-normalized REE pattern of NWA 7188. The bulk composition shows a LREE-enriched and HREE-depleted pattern with pronounced negative Eu anomaly, whose La, Eu, and Lu concentrations are $22 \times \text{CI}$, 13

× CI, and 16 × CI, respectively. As well as Hf, the concentrations of Zr (89.48 µg/g), Nb (6.40 µg/g), and Ta (0.33 µg/g) are higher than those of the main-group–Nuevo Laredo-group eucrites, but are consistent with those of the Stannern-group eucrites. The Zr/Hf and Nb/Ta ratios of basaltic eucrites range from 33.9 to 40.9 and from 17.0 to 20.9, respectively (Barrat et al. 2000, 2007; Jochum et al. 2000; Weyer et al. 2002; Münker et al. 2003; Roszjar et al. 2011), which are similar to the chondritic ratios (Zr/Hf = 34.3 ± 0.3, Nb/Ta = 19.9 ± 0.6; Münker et al. 2003). The Zr/Hf (= 36.0) and Nb/Ta (= 19.6) ratios of NWA 7188 are within the range of those for basaltic eucrites.

Oxygen Isotope Compositions

Figure 6 shows the oxygen isotope composition of NWA 7188 obtained in this study along with the data for other HED meteorites compiled by Greenwood et al. (2017). The $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$ values of NWA 7188 are $1.968 \pm 0.008\text{‰}$ (2σ), $4.224 \pm 0.016\text{‰}$ (2σ), and $-0.245 \pm 0.016\text{‰}$ (2σ), respectively. The $\Delta^{17}\text{O}$ value for NWA 7188 is within error of the mean eucrite value of $-0.240 \pm 0.018\text{‰}$ (2σ) (Greenwood et al. 2017).

^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd Isochron Ages

Sm and Nd concentrations and Nd isotope ratios are presented in Table 3. The data for the G1 fraction was reported in Kagami and Yokoyama (2016). All the data from each fraction plot on a single line within the analytical uncertainties in both of ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd isochron diagrams (Figs. 7a and 7b). The ^{147}Sm – ^{143}Nd isochron yields an age of 4582 ± 190 Ma (2σ , MSWD = 1.1) with an initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50662 ± 0.00025 . In contrast, the slope of ^{146}Sm – ^{142}Nd isochron provides the $^{146}\text{Sm}/^{144}\text{Sm}$ ratio (R_{Sm}) of 0.00757 ± 0.00093 (2σ , MSWD = 1.9) at the formation of NWA 7188. To derive the ^{146}Sm – ^{142}Nd isochron age of NWA 7188 from the observed R_{Sm} , the half-life of ^{146}Sm ($= t_{1/2}^{146}$) and the initial Solar System $^{146}\text{Sm}/^{144}\text{Sm}$ ratio ($= R_{\text{Sm}}^0$) are required. In this study, we adopted $t_{1/2}^{146} = 103$ Myr and $R_{\text{Sm}}^0 = 0.00828 \pm 0.00044$ (Marks et al. 2014) for calculation of ^{146}Sm – ^{142}Nd age of NWA 7188. Consequently, the obtained R_{Sm} of NWA 7188 corresponds to an age of 4554^{+17}_{-19} Ma, with an initial Nd isotope ratio of $^{142}\text{Nd}/^{144}\text{Nd} = 1.141511 \pm 0.000035$. The ^{146}Sm – ^{142}Nd age of NWA 7188 is the oldest age measured for the subset of basaltic eucrites for which ^{146}Sm – ^{142}Nd ages have been obtained.

DISCUSSION

Effect of Terrestrial Weathering

It has been reported that some Saharan meteorites occasionally show elevated Sr and Ba concentrations as a result of terrestrial weathering that caused the formation of secondary carbonates and sulfates within the meteorites (Croizat et al. 2003). For this reason, Sr and Ba concentrations can be useful as a means of evaluating the extent of terrestrial weathering in desert meteorites. In addition, Th/U and Hf/Sm ratios in meteorites have been used to investigate the extent of terrestrial aqueous alteration in a particular sample (Barrat et al. 2003, 2007). This is because U and Sm are fluid mobile elements compared to Th and Hf, respectively, while these ratios are not changed significantly by magmatic processes due to the similar incompatibilities of each pair of elements. In fact, the Th/U ratio in eucrites including weathered meteorites ranges from 1.9 to 7.2 (Mittlefehldt and Lindstrom 1991; Yamaguchi et al. 2009), with this variation being twice as large as that for fall eucrites (2.7–5.1; Barrat et al. 2003). Additionally, the Hf/Sm ratio of Antarctic eucrites (0.5–3.2; Mittlefehldt and Lindstrom 1991) are variable compared with that of unweathered eucrites (0.6–1.0; Barrat et al. 2003).

The measured Sr (132 $\mu\text{g/g}$) and Ba (69 $\mu\text{g/g}$) concentrations in NWA 7188 are substantially higher than those determined for either fall or Antarctic basaltic eucrites (Sr: ~70 to ~100 $\mu\text{g/g}$, Ba: ~15 to ~60 $\mu\text{g/g}$; Barrat et al. 2003). This indicates that the influence of terrestrial weathering on this meteorite persists despite the use of the acetone–H₂O washing procedure. On the other hand, the ratios of Th/U (= 3.1) and Hf/Sm (= 0.8) in NWA 7188 are within the range of unweathered eucrites. These results indicate that terrestrial weathering of NWA 7188 in a hot desert environment has increased the concentration of Sr and Ba without modifying the Th/U and Hf/Sm ratios. Therefore, we consider that the concentrations of U, Sm, and possibly the rest of REEs have not been redistributed among minerals in NWA 7188 via terrestrial alteration, in which case the concentrations of these elements in the bulk rock and individual minerals of NWA 7188 represent the original values that were acquired on the meteorite parent body.

Classification of NWA 7188

The Fe/Mn ratio of pyroxene and the oxygen isotopic composition of basaltic eucrites have been widely used as a means of evaluating potential genetic links between basaltic eucrites. Previous studies argued that pyroxene in Ibitira exhibits higher Fe/Mn ratios (33–39; 36.4 on average) than has been measured in the other basaltic eucrites (30 \pm 2) (Papike et al. 2003; Mittlefehldt 2005). In addition, Ibitira has a distinct oxygen isotopic composition compared to other eucrites (Wiechert et al. 2004). These

observations have led researchers to conclude that Ibitira originated from a parent body other than Vesta (Mittlefehldt 2005). Although basaltic achondrites, Pasamonte and Caldera, have pyroxene Fe/Mn ratios indistinguishable from other basaltic eucrites, their oxygen isotope compositions are different from those of the other eucrites (Wiechert et al. 2004). The consistency of the Fe/Mn ratios of pyroxene and oxygen isotope composition in NWA 7188 with those of the other basaltic eucrites indicates that NWA 7188 is a normal member of HED meteorites and as a consequence most likely originated from Vesta.

On a diagram of TiO_2 concentration vs. FeO/MgO ratio, the main-group, Nuevo Laredo-group, and Stannern-group eucrites plot in different fields, with the TiO_2 concentrations of the Stannern-group eucrites being higher than those of the main-group–Nuevo Laredo-group eucrites (e.g., Stolper 1977; Warren and Jerde 1987). Therefore, this diagram has been used to distinguish the chemical groups of basaltic eucrites (e.g., Barrat et al. 2000; Mittlefehldt 2015). As shown in Fig. 4a, NWA 7188 has a higher Ti concentration than those of the main-group–Nuevo Laredo-group eucrites and plots within the field of Stannern-group eucrites. As well as TiO_2 concentration, diagrams of La and Hf concentration vs. FeO/MgO ratio can also be used to discriminate between the various chemical groups of basaltic eucrites (e.g., Barrat et al. 2000; Mittlefehldt 2015). The La vs. FeO/MgO and Hf vs. FeO/MgO diagrams indicate that NWA 7188 has much higher La and Hf concentrations than those of the main-group–Nuevo Laredo-group eucrites at a given FeO/MgO (Figs. 4b and 4c). Based on the diagrams of Ti, La, and Hf concentrations vs. FeO/MgO ratios, NWA 7188 can be unambiguously classified as a member of the Stannern group of eucrites.

The various chemical groups of basaltic eucrites are also distinguishable by their REE patterns. Figure 5 shows the REE pattern for NWA 7188 in relation to various representative eucrites from each of the main chemical group. The main-group eucrites have a flat REE pattern with no Eu anomaly, and their REE concentrations are $\sim 11 \times \text{CI}$. In contrast, the REE patterns of Nuevo Laredo-group and Stannern-group eucrites are characterized by LREE-enriched and HREE-depleted patterns with pronounced negative Eu anomalies. In detail, these two groups can be distinguished by the differences in the degree of Eu anomaly and the slope from Gd to Lu ($\text{Gd}_\text{N}/\text{Lu}_\text{N}$) in the REE pattern. The Stannern-group eucrites have lower Eu/Eu^* (0.57–0.67) and higher $\text{Gd}_\text{N}/\text{Lu}_\text{N}$ ratios (1.26–1.31) compared to the Nuevo Laredo-eucrites ($\text{Eu}/\text{Eu}^* = 0.76\text{--}0.78$ and $\text{Gd}_\text{N}/\text{Lu}_\text{N} = 1.05\text{--}1.16$) (Barrat et al. 2011; Roszjar et al. 2011). The observation that the Eu/Eu^* and $\text{Gd}_\text{N}/\text{Lu}_\text{N}$ ratios of NWA 7188 (0.64 and 1.26, respectively; Table 2) are within the range of the Stannern-group eucrites reinforces the likelihood that NWA 7188 is a new member of

the Stannern-group.

The oxygen isotope ratios of five Stannern-group eucrites measured to date indicate that there is no significant difference between members of the Stannern-group and the main-group–Nuevo Laredo-group eucrites (Fig. 6) (Clayton and Mayeda 1996; Wiechert et al. 2004; Greenwood et al. 2005; Barrat et al. 2007; Roszjar et al. 2011). In support of this observation, the oxygen isotope composition of NWA 7188 measured in this study falls within the $\Delta^{17}\text{O}$ range measured for the main-group–Nuevo Laredo-group eucrites (Fig. 6). NWA 7188 has a slightly elevated $\delta^{18}\text{O}$ composition compared with the majority of eucrites plotted in Fig. 6, which may reflect the influence of terrestrial weathering. However, in terms of its $\delta^{18}\text{O}$ value NWA 7188 plots within the range of values measured in other eucrites (Greenwood et al. 2017) and so the extent of terrestrial weathering is relatively limited.

Geochemical Characteristics of NWA 7188 as a Stannern-Group Eucrite

Approximately ten Stannern-group eucrites have been identified to date based on the diagrams of Ti, La, and Hf concentrations vs. FeO/MgO ratios, and/or the Mg# (= molar $100 \times \frac{\text{MgO}}{\text{FeO}+\text{MgO}}$) and REE compositions (Mittlefehldt 2015). NWA 7188 and some representative Stannern-group eucrites, such as Stannern, Bouvante, NWA 4523, NWA 5073, and Yamoto (Y)-75011 have variable REE concentrations that are characterized by enhanced LREE/HREE ratios with negative Eu anomalies (Fig. 5). In particular, NWA 7188 has similar modal REE abundances and pattern (Eu/Eu*: 0.64, Gd_N/Lu_N: 1.26, and La_N/Sm_N: 1.00) to those of Stannern (0.65, 1.26, and 1.00, respectively) when compared to those of the other Stannern-group eucrites (0.58–0.68, 1.30–1.35, and 1.02–1.08, respectively).

Among the representative Stannern-group eucrites shown in Fig. 5, Stannern, Bouvante, and NWA 4523 are monomict basaltic eucrites. In contrast, NWA 5073 is an unbrecciated basaltic eucrite that contains large pyroxene phenocrysts with different modal abundances of pyroxene (64.7 vol.%) and plagioclase (26.4 vol.%) (Roszjar et al. 2011) compared with those of the other basaltic eucrites (51.2 and 43.3 vol.%, respectively; Delaney et al. 1984). Additionally, Roszjar et al. (2016) reported that the ^{182}Hf – ^{182}W dates of some zircons in NWA 5073 yielded younger ages down to ~4530 Ma, which led the authors to suggest that NWA 5073 may have experienced a reheating event. Therefore, the relatively low REE concentration of NWA 5073 may not be representative of the original chemical composition of Stannern-group eucrites. On the other hand, Y-75011 is a polymict breccia and contains a variety of pyroxene fragments, including

Binda-type (cumulate eucrite) and Juvinas-type pyroxenes (Takeda et al. 1979). The lower REE concentration of Y-75011 compared to the monomict Stannern group suggests the incorporation of various clasts with non-Stannern group chemical compositions. In addition to Y-75011, a polymict Stannern-group eucrite Y-74450 shows lower REE concentrations than the other monomict Stannern group (Shimizu and Masuda 1986). In summary, the evidence seems to point to Stannern, Bouvante, and NWA 4523 as being relatively pristine examples of monomict Stannern-group eucrites and appear to preserve the original chemical composition of the Stannern group. Given that NWA 7188 is a monomict Stannern-group eucrite, with a similar modal abundance and REE pattern to Stannern, it is also clearly a member of this relatively pristine group. This evidence indicates that NWA 7188 also preserves the initial composition of the Stannern-group eucrites.

In addition to the similarity of the major and trace element compositions, the metamorphic grades of NWA 7188, Stannern, and Bouvante all belong to type 4 (Takeda et al. 1983; Michel-Lévy et al. 1987). Taking the geochemical and petrological evidence into account, these three Stannern-group eucrites are believed to have been formed by a similar process and probably experienced similar thermal metamorphism. However, the ^{81}Kr exposure ages of Stannern and Bouvante are 35.1 ± 0.7 Ma and 6.7 ± 0.4 Ma respectively, which are clearly different from each other (Shukolyukov and Begemann 1996; Miura et al. 1998). This result might indicate that they were ejected from Vesta by different impact events and consequently different regions of Vesta. It is currently not known whether NWA 7188 is related to either the Stannern or Bouvante ejection event or to a third distinct event. Further study and in particular determining the exposure ages for NWA 7188 and other Stannern-group eucrites will provide new insights into the distribution of the Stannern-group eucrites on Vesta.

Chronology of Eucrites

Review of Chronological Studies on Eucrites

Some short-lived chronometers have shown that the accretion, core–mantle differentiation, silicate differentiation (crustal formation), and initial crystallization of basaltic magmas on Vesta started within a few million years after CAI formation. Here, we focus on monomict eucrites and exclude from the chronological discussion ages determined for polymict eucrites. This is because polymict eucrites are mixtures of more than two different rock types (e.g., sub-groups of basaltic eucrites) and so the chronological evidence they furnish may not be related to actual events in the history of their parent body. The timing of core–mantle segregation for Vesta has been estimated to

be within ~1 Myr after CAI formation on the basis of the ^{182}Hf – ^{182}W systematics (Touboul et al. 2015). The silicate differentiation followed the core–mantle segregation and occurred at 4564.8 ± 0.9 Ma according to ^{53}Mn – ^{53}Cr whole-rock isochron data (Lugmair and Shukolyukov 1998). This timing was also recorded by the ^{26}Al – ^{26}Mg whole-rock isochron age of eucrites, which was $2.88^{+0.14}_{-0.12}$ Myr after CAI formation (Hublet et al. 2017). The ^{53}Mn – ^{53}Cr ages obtained from inter-mineral isochrons of Juvinas, Chervony Kut, and Asuka (A)-881394 yielded 4562.5 ± 1.0 Ma, 4563.6 ± 0.9 Ma, and 4564 ± 2 Ma, respectively (Lugmair and Shukolyukov 1998; Nyquist et al. 2003). The ^{26}Al – ^{26}Mg inter-mineral isochrons of eucrites was determined to be 2–3 Myr after CAI formation (Schiller et al. 2010; Hublet et al. 2017). These ages suggest that the igneous crystallization of basaltic magmas began simultaneously with crust formation on Vesta.

The period of initial crystallization of basaltic crust has been discussed based on the ^{207}Pb – ^{206}Pb zircon dates for basaltic eucrites. Because the ^{207}Pb – ^{206}Pb dates of eucritic zircons have clustered around 4550 Ma, the volcanism on Vesta is considered to have lasted until around 4550 Ma (e.g., Misawa et al. 2005; Zhou et al. 2013) (Fig. 8a). In contrast, some zircons found in highly metamorphosed basaltic eucrites are recognized to have formed during subsolidus reheating caused by global metamorphism (Haba et al. 2014; Roszjar et al. 2014). Iizuka et al. (2015) argued that the ^{207}Pb – ^{206}Pb date of zircons in a highly metamorphosed basaltic eucrites Agoult (4554.5 ± 2.0 Ma) corresponds to the timing of global metamorphism on Vesta. Thus, the global metamorphism on Vesta may have occurred contemporaneously with the initial crystallization of eucrite magmas during the very early stages of Vesta’s evolution, most likely due to the internal heat of deeply buried lavas (Yamaguchi et al. 1996, 1997).

^{207}Pb – ^{206}Pb or ^{182}Hf – ^{182}W zircon dates for only two monomict Stannern-group eucrites, Stannern and NWA 4523, have been reported. The ^{207}Pb – ^{206}Pb zircon date for Stannern was 4550 ± 10 Ma (Ireland and Bukovanská 1992). This age would correspond to the timing of volcanism or the global metamorphism because we cannot identify the characteristics of zircons reported by Ireland and Bukovanská (1992), whereas Stannern contains zircons formed during the global metamorphism (Haba et al. 2014). In addition, the ^{182}Hf – ^{182}W dates for zircons from the Stannern-group eucrite NWA 4523 ranged from 4558 to 4565 Ma (Roszjar et al. 2016). This age corresponds to the timing of initial crystallization of basaltic crust because the ^{182}Hf – ^{182}W system in zircon is not reset by later metamorphism due to its high closure temperature (~1400 °C). The observed overlapping of zircon dates from the Stannern-group (4550–4565 Ma) and the main-group eucrites, of which the weighted mean ^{207}Pb – ^{206}Pb age yielded 4553.4 ± 2.6 Ma, suggests that the initial crystallization and global metamorphism of the Stannern-group

euclites took place during the same period as the main-group euclites.

The Sm–Nd ages of a few basaltic euclites have given dates older than 4.53 Ga (Lugmair 1974; Lugmair and Galer 1992; Wadhwa and Lugmair 1996; Kumar et al. 1999), whereas some basaltic euclites record much younger ^{146}Sm – ^{142}Nd and ^{147}Sm – ^{143}Nd ages of 4.40–4.53 Ga (Lugmair and Scheinin 1975; Nyquist et al. 1986, 1997; Wadhwa and Lugmair 1995; Tera et al. 1997; Yamaguchi et al. 2001) (Fig. 8b). The earlier date appears to represent the timing of igneous activity and global metamorphism on Vesta and was apparently not disturbed by later short-term reheating events, as indicated by the consistent range of the ^{207}Pb – ^{206}Pb dates for eucritic zircons. Numerical simulations of the thermo-chemical evolution of Vesta (Neumann et al. 2014), suggest that the temperature of Vesta’s eucritic upper crust (~20 km thick) (Mandler and Elkins-Tanton 2013), was <~600 °C at ~30 Ma after CAI formation. The internal heat source of the igneous activity and global metamorphism, from the decay of short-lived ^{26}Al , was absent in the upper crust of Vesta at that time. Thus, the observed young ages indicate that the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ decay system of some basaltic euclites was likely disturbed during secondary events such as impact on Vesta.

The ^{244}Pu –Xe ages reported by previous studies (Michel and Eugster 1994; Shukolyukov and Begemann 1996; Miura et al. 1998; Park and Nagao 2005) suggest that the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ and ^{244}Pu –Xe ages are generally in reasonable agreement with each other (Fig. 8c). The $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ and ^{244}Pu –Xe systems were affected to the same degree by resetting during impact reheating (Figs. 8b and 8c). In general, mineral closure temperatures of pyroxene and plagioclase for the U–Pb system (~800 °C; Iizuka et al. 2014) are lower than those for the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ system, suggesting that the ^{207}Pb – ^{206}Pb ages are less resistant to resetting by local reheating and/or impact events than $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ ages. Actually, all of the ^{207}Pb – ^{206}Pb ages for basaltic euclites derived from the whole rock and mineral samples are younger than 4.53 Ga (Fig. 8d). Overall, the younger $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$, ^{244}Pu –Xe and U–Pb ages suggest that the reheating events postdated the initial crystallization and global metamorphism, and although the temperatures attained were subsolidus, they were also high enough to reset the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$, ^{244}Pu –Xe, and U–Pb systems for bulk rocks and minerals, with the exception of zircons.

The ^{146}Sm – ^{142}Nd Chronology of NWA 7188

Sm–Nd systematics provide two chronometers that utilize long-lived ^{147}Sm ($t_{1/2} = 106$ Gyr) with a daughter nuclide ^{143}Nd and short-lived ^{146}Sm ($t_{1/2} = 103$ Myr) with a daughter nuclide ^{142}Nd . In some situations, the ^{147}Sm – ^{143}Nd ages of euclites can be

significantly affected by secondary events, whereas the ^{146}Sm – ^{142}Nd systematics is undisturbed (Prinzhofer et al. 1992; Wadhwa et al. 2006). Prinzhofer et al. (1992) suggested that the ^{147}Sm – ^{143}Nd systematics can be disturbed by partial re-equilibration of plagioclase and phosphates that episodically occur within a short period of time, whereas the ^{146}Sm – ^{142}Nd age are not affected by such a re-equilibration event. Hereafter, we discuss the Sm–Nd chronology of NWA 7188 by using the ^{146}Sm – ^{142}Nd age (4554^{+17}_{-19} Ma).

As noted above (see the Review of Chronological Studies on Eucrites in this section), the thermal evolution of Vesta was discussed based on chronological data reported in previous works. Because the ^{146}Sm – ^{142}Nd age of NWA 7188 is in good agreement with the timing of the initial crystallization or global metamorphism at ~4.55 Ga, the Sm–Nd decay system was not disturbed by this later reheating such as by intermittent impact events. Therefore, NWA 7188 is also a rare and important basaltic eucrite with respect to the chronological information it can furnish about Vesta's early evolution.

Closure Temperature of the Sm–Nd System in NWA 7188

The Sm–Nd closure temperatures for pyroxene and plagioclase have not been quantitatively discussed in the literature to date, while those in other minerals such as garnet have been examined in detail in previous studies (e.g., Tirone et al. 2005; Scherer et al. 2010). To evaluate the degree of isotopic resetting in the ^{147}Sm – ^{143}Nd chronometer, Nyquist et al. (1991a, b) compared three ^{147}Sm – ^{143}Nd internal isochrons consisting of plagioclase (density <2.85 g/cm³) and pyroxene (density = 3.45 – 3.55 g/cm³ and 3.55 – 3.7 g/cm³) minerals and whole rock that were prepared from unheated, moderately (790 °C) heated and heavily (990 °C) heated samples of a lunar basalt 15555. The results showed that the ^{147}Sm – ^{143}Nd isochron of the heavily heated samples had been disturbed, while that of the moderately heated samples appeared to be only slightly perturbed compared to the unheated samples. Thus, Sm–Nd systematics would be reset by heating at the subsolidus temperatures of basaltic eucrites (<1060 °C; Stolper 1977).

In order to better constrain the thermal event that corresponds to the ^{146}Sm – ^{142}Nd age obtained for NWA 7188, we have estimated the Sm–Nd closure temperature of the constituent minerals of basaltic eucrites in two different ways, as discussed below. First, we compare the Sm–Nd ages with the ^{207}Pb – ^{206}Pb ages of whole rock and minerals (pyroxene and plagioclase) and the ^{207}Pb – ^{206}Pb dates of zircons among basaltic eucrites. Some basaltic eucrites have Sm–Nd ages that appear to correspond to the initial magmatism or metamorphism at around 4550 Ma. In contrast, all of the ^{207}Pb – ^{206}Pb whole rock and mineral ages are younger than 4530 Ma (Figs. 8b and 8d). On the other hand,

the Sm–Nd ages of some basaltic eucrites are also much younger than 4530 Ma, while most of the ^{207}Pb – ^{206}Pb dates of eucritic zircons are older than 4530 Ma (Figs. 8a and 8b). These comparisons reveal that the closure temperature of the Sm–Nd decay system is higher than that of the U–Pb system for whole rocks and minerals, but lower than that of eucritic zircons. Then, the Pb closure temperatures in plagioclase, pyroxene, and zircon of basaltic eucrites are estimated to constrain the Sm–Nd closure temperature by adapting the cooling rate and grain size of basaltic eucrites. We note the data required to calculate the closure temperature as follows. The diffusion coefficients of Pb (D_{Pb}) in plagioclase, pyroxene (augite), and zircon used in the calculation are given as follows (Cherniak 1995; 2001; Cherniak and Watson 2003);

$$D_{\text{Pb in plagioclase}} = 3.75 \times 10^{-6} \times e^{-327 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

$$D_{\text{Pb in pyroxene}} = 3.8 \times 10^{-5} \times e^{-372 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

$$D_{\text{Pb in zircon}} = 1.1 \times 10^{-1} \times e^{-550 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}$$

where R and T are the gas constant and temperature, respectively. Although there are two different Pb diffusion coefficients for zircon (Lee et al. 1997; Cherniak and Watson 2003), we use that from Cherniak and Watson (2003) to obtain the maximum closure temperature of U–Pb decay system in zircon. The closure temperature is given by employing the formalism developed by Dodson (1973);

$$T_c = \frac{E/R}{\ln \left(\frac{ART_c^2 D_0 / a^2}{E \, dT/dt} \right)}$$

where E and D_0 are the activation energy and pre-exponential factors for diffusion of the relevant species, A is a geometric factor ($A = 55$ for spherical geometry), dT/dt is the cooling rate, and a is the effective diffusion radius. It should be noted that the cooling rate for the U–Pb decay system for whole rocks and minerals depends on the thermal event that caused the resetting of the system. According to Haba et al. (2019), the Pb–Pb ages of whole rocks and minerals probably correspond to a large-scale collision on Vesta 4525.4 Ma. Although the cooling rate during the collision has not been estimated, it should have been slower than that of a local impact due to heat insulation by the collisional debris. In the calculation, we utilize the cooling rate during the extensive metamorphism (0.01 °C/year) obtained from a basaltic eucrite, Sioux County (metamorphic grade: type 5) (Miyamoto et al. 1996). This estimate should provide the minimum closure temperature of U–Pb decay system of whole rock and minerals. The effective diffusion radius is assumed to be 125 μm for plagioclase and pyroxene and 8 μm for zircon, because most basaltic eucrites have fine- to medium-grained pyroxene and

plagioclase (McSween et al. 2011) and zircon grain sizes are a few–30 μm (Haba et al. 2014). The closure temperature of Pb is estimated to be $\sim 855^\circ\text{C}$ for plagioclase and $\sim 930^\circ\text{C}$ for pyroxene, whereas that for zircon is $\sim 1040^\circ\text{C}$. Therefore, the Sm–Nd closure temperature of basaltic eucrites is most likely to be between $\sim 855^\circ\text{C}$ and $\sim 1040^\circ\text{C}$.

Second, we estimate the Sm–Nd closure temperature of NWA 7188 by the diffusion calculation as well as those for Pb closure temperature above. Ganguly et al. (1998) reported that the diffusion coefficient of Sm (D_{Sm}) in garnet is 5–10% larger than that of Nd (D_{Nd}) because of the smaller ionic radius of Sm (1.09 Å) compared to Nd (1.12 Å). Although the D_{Sm} values for pyroxene and plagioclase at $\sim 1000^\circ\text{C}$ are not available at present, it is conceivable that the D_{Sm} values for these minerals are also $\sim 10\%$ higher than the D_{Nd} values. Therefore, we estimate the closure temperature of the Sm–Nd system for plagioclase and pyroxene using the D_{Nd} values of the minerals that were used for deriving the Sm–Nd isochron age. The D_{Nd} in plagioclase used in the calculation is given as follows (Cherniak 2003);

$$D_{\text{Nd in plagioclase}} = 5.9 \times 10^{-6} \times e^{-398 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}.$$

Sano et al. (2011) argued that the D_{Nd} in pyroxene (enstatite) are given as follows;

$$D_{\text{Nd in pyroxene}} = 9.2 \times 10^{-13} \times e^{-222 \text{ KJ mol}^{-1}/RT} \text{ m}^2 \text{ s}^{-1}.$$

The diffusion equation and parameters excluding effective diffusion radius are the same as those used in the calculation of Pb closure temperature above. The effective diffusion radius of 22.5 μm was employed for both plagioclase and pyroxene, because the minimum grain size of mineral fraction used for the Sm–Nd isochron of NWA 7188 is 45 μm (G3 fraction). Although the G4 fraction includes grains smaller than 45 μm in diameter, these small grains are probably fragments of original minerals. Indeed, almost all of the pyroxene and plagioclase observed in NWA 7188 are much larger than 45 μm (Fig. 1a). Therefore, the closure temperature that we discuss here is the minimum value and the most rigorous estimate available. As shown in Fig. S3, the closure temperatures of Nd are estimated to be $\sim 965^\circ\text{C}$ for plagioclase and $\sim 865^\circ\text{C}$ for pyroxene. Even if the D_{Sm} for plagioclase and pyroxene are 10% larger than D_{Nd} of these minerals. The resulting closure temperatures for Sm are not significantly different from those of Nd. The Sm–Nd closure temperatures obtained for NWA 7188 are consistent with those predicted from the heating experiment using lunar basalt (Nyquist et al. 1991b) and the chronological comparison among the Sm–Nd and U–Pb ages of whole rock and minerals and U–Pb dates of zircons.

According to the estimated closure temperatures of Sm–Nd system for plagioclase and pyroxene by the two different procedures as discussed above, it appears that the

global metamorphism could not completely reset the Sm–Nd system in NWA 7188 because it has been reported that eucrites with the metamorphic grade of type 4 experienced metamorphism at ~800 °C (Barrat et al. 2007). Therefore, it is likely that the ^{146}Sm – ^{142}Nd age obtained in this study corresponds to the timing of initial crystallization of basaltic magmas, although partial resetting of the ^{146}Sm – ^{142}Nd age due to global metamorphism cannot be rejected completely.

Concluding remarks

In this study, we performed textual observations, geochemical and chronological studies on a basaltic eucrite NWA 7188. The textual observations and chemical composition of pyroxene and plagioclase revealed that NWA 7188 is a monomict basaltic eucrite. The augite lamella in pigeonite showed Ca-zoning, which indicates that the metamorphic grade of NWA 7188 is defined as type 4. The oxygen isotope composition confirmed that NWA 7188 was derived from the same parent body as that of the HED clan. The CI chondrite-normalized REE pattern demonstrated a LREE-enriched and HREE-depleted pattern with a distinct negative Eu anomaly. Because this REE pattern is consistent with those of the Stannern-group eucrites, NWA 7188 is considered to be a new Stannern-group eucrite. This result is also supported by the higher Hf and Ti concentrations than those of the main-group basaltic eucrites. The ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd mineral isochrons for NWA 7188 yielded ages of 4582 ± 190 and 4554^{+17}_{-19} Ma, respectively. The closure temperature of $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ systems calculated in this study suggests that the $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ decay system for NWA 7188 has not been totally reset during global metamorphism on Vesta. Therefore, we conclude that the ^{146}Sm – ^{142}Nd age of NWA 7188 corresponds to the timing of initial crystallization of the basaltic magmas that formed the Stannern-group eucrites or shows the partially reset age during the global metamorphism.

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Figure Caption

Fig. 1. Back-scattered electron images of NWA 7188. (a) Pyroxene and plagioclase grains in the FG area. (b) Mesostasis area in the NWA 7188. (c) The largest zircon and surrounding minerals. (d) Thick and dense augite lamellae in the rim (dark gray) and thin lamellae in the core. White is opaque minerals and black is cracks and/or holes. Mineral abbreviations are as follows: pyx = pyroxene, plag = plagioclase, and ilm = ilmenite.

Fig. 2. Compositions of major minerals in NWA 7188 plotted in the part of triangle diagram. Minerals in the FG and CG areas are shown as red squares and blue circles, respectively. (a) Pyroxene compositions. (b) Plagioclase compositions.

Fig. 3. Diagram of Mn vs. Fe (atoms per six-oxygen formula unit: afu) for pyroxene in NWA 7188. Minerals in the FG and CG areas are shown as red squares and blue circles, respectively. Slope (= 0.031) of the correlation corresponds to the Fe/Mn ratio of 32.3.

Fig. 4. (a) TiO₂ (b) La and (c) Hf vs. FeO/MgO plots for NWA 7188 and various basaltic eucrites. In these plots, basaltic eucrites are distinguished into three different groups (main group, Nuevo Laredo group, and Stannern group). The FeO concentration is calculated as the total of Fe content. The data excluding NWA 7188 are taken from the compiled data of Mittlefehldt (2015).

Fig. 5. CI chondrite-normalized REE patterns of NWA 7188 (red square) and the other basaltic eucrites. Open diamond (Y-75011), gray diamond (NWA 5073), open square (Bouvante), gray triangle (NWA 4523), and inverted triangle (Stannern) are Stannern-group eucrites. Nuevo Laredo and Juvinas (main-group eucrite) are shown as open circles and open triangles, respectively. The REE compositions other than NWA 7188 are obtained from Barrat et al. (2003), Barrat et al. (2007), and Roszjar et al. (2011). The reference of CI chondrite compositions is obtained from McDonough and Sun (1995).

Fig. 6. Oxygen three isotope plot showing the data for NWA 7188 (this study) and the other basaltic eucrites (Greenwood et al. 2017). Symbols are the same as Fig. 4. Gray field is 2 σ of the data for eucrites and diogenite, falls only, and the eucrite fractionation line (EFL) is shown as dashed line of $\Delta^{17}\text{O} = -0.240 \pm 0.014$ (2 σ)

(Greenwood et al. 2017).

Fig. 7. (a) ^{147}Sm – ^{143}Nd and (b) ^{146}Sm – ^{142}Nd isochron diagrams of NWA 7188. Isochron and error envelope are shown as solid line and dashed curves, respectively. Error bars are 2SE. Some error bars are smaller than the size of symbols. MSWDs of the ^{147}Sm – ^{143}Nd and ^{146}Sm – ^{142}Nd isochrons are 1.1 and 1.9, respectively.

Fig. 8. Comparison of eucrite ages dated by various chronometers. Histogram (gray field) and probability density curve (black curve) of (a) ^{207}Pb – ^{206}Pb dates for zircons from monomict basaltic eucrites, (b) $^{147,146}\text{Sm}$ – $^{143,142}\text{Nd}$ mineral isochron ages for monomict basaltic eucrites, (c) ^{244}Pu – ^{136}Xe mineral isochron ages for monomict basaltic eucrites, and (d) ^{207}Pb – ^{206}Pb ages for monomict basaltic eucrites. Probability density curve is not shown for Sm–Nd age because of the shortage of data. Red dashed line indicates the ^{146}Sm – ^{142}Nd age of NWA 7188. The ^{146}Sm – ^{142}Nd isochron ages are recalculated using the ^{146}Sm half-life and the Solar System initial $^{146}\text{Sm}/^{144}\text{Sm}$ ratio of Marks et al. (2014). The ages used for (a), (b), (c), and (d) are summarized in Table S2.